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## Synthesis of Diamond Films with Pulsed Plasmas

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Diamond films were grown in plasmas formed with microwaves that were modulated with a pulse generator. Films obtained with the use of pulse periods in the nanosecond, microsecond, and millisecond ranges were compared to baseline films which were obtained with a CW plasma. The deposited films were examined with SEM, XRD and Micro-Raman spectroscopy. For the experimental conditions used, the diamond films' growth rates and quality improved with increasing pulse duration while maintaining a duty cycle at nearly 50 percent, and reached a maximum with CW generated films. This was attributed primarily to an increasing degree of supersaturation of atomic hydrogen at the growth surface with increasing pulse time.

### I. INTRODUCTION

The metastable growth of diamond films has been achieved by a number of continuous plasma-enhanced chemical vapor deposition (CVD) methods [1-4]. Of these, none have gained more attention than the CW microwave plasma-enhanced chemical vapor deposition technique [4]. In this technique the amount of microwave power used is typically limited by the extent of substrate heating induced by plasma and microwave heating. Concomitantly, this restriction in the amount of microwave power that can be used also reduces the amount of reactants that can be dissociated which may adversely effect the film's growth rate as well as quality.

The use of pulsed radio-frequency discharges of very high power to deposit thin films has recently been reported by Scarsbrook et al. [5]. They found that short pulses at high power resulted in increased reactant dissociation rates while simultaneously reducing substrate heating. This resulted in higher deposition rates at lower temperatures than previously obtained by steady state conditions. In this paper we investigate the use of microwave induced pulsed plasmas in the CVD growth of diamond films.

### II. EXPERIMENTAL PROCEDURE

A microwave plasma-enhanced CVD system with a dielectric waveguide was used in the deposition of the diamond films. A schematic of the system used is shown in Figure 1. The use of dielectric waveguides to form plasmas has been described previously [6]. The microwave supply was modified by the addition of a Phillips PM5715 pulse generator for pulse operation, and the maximum power output was increased by an order of magnitude to 2.5KW at  $7.36 \pm 0.050$  GHz from that previously reported, with the use of an Energy Systems 2.5KW, Low X-Band Amplifier.

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Deposition was performed on (100) silicon n-type substrates. To aid in the nucleation and reduce the time necessary to nucleate the diamond film, the substrates were seeded by abrading them with diamond crystals that were up to 2 micrometers in size. The dielectric waveguide, located within the inner chamber, is maintained at atmospheric pressure. The silicon substrates were placed horizontally on sapphire tiles that rested on the inner chamber just above the output end of the dielectric waveguide. In addition Grafoil, a graphite sheet product of EGC Corporation, was placed about the substrate. These procedures were used to suppress unwanted plasma reactions and minimize any potential contamination of the diamond film.

After the deposition tube was evacuated to less than 100 millitorr, argon was introduced into the reaction chamber and the plasma initiated when the pressure was about 5 torr. Oxygen, and then hydrogen were introduced into the reaction chamber. The deposition pressure was first set by using a throttle valve, and then adjusted with a vernier controlled metering valve. The plasma's intensity was greatest at the surface of the substrate and decreased with distance from the surface. Depositions were performed with and without the use of external heating. When a furnace was not used the substrate was heated only by the plasma and microwave heating. Substrate temperatures were measured with a Chapin Tec, Model ROS-5U two color optical pyrometer. The temperature deposition range was between 800 and 1050°C with an average substrate temperature of 925°C.

The gas flow rates during deposition were 100 cc/min hydrogen, 0.5 cc/min methane, and 0.5 cc/min oxygen. In addition argon, which acted as a diluent, was added to the gas flow in the amounts of 100 cc/min for CW and 50 cc/min for pulsed-plasma depositions respectively. The pulse generator was run in the nanosecond, microsecond, and millisecond ranges. The Energy Systems klystron amplifier was set to obtain the system's peak power for all pulsed-plasma depositions. Duty cycles were adjusted to about 50 percent, to obtain an average forward power that was similar to the power used in CW baseline depositions. An effort was made to maintain the substrate at a deposition temperature similar to that of the CW baseline. Deposition times were between 7 and 8 hours.

### III. RESULTS

Some remarks are in order concerning the pulsing of microwaves and the resulting plasmas. Plasmas formed with pulse repetition rates in the nanosecond range were continuous. Plasmas formed in the microsecond and millisecond ranges were pulsed. In addition, the rise and fall time of the microwave system was approximately 40 nanoseconds, primarily due to the narrow bandwidth of the klystron amplifier. As a result, in nanosecond pulsed experiments the peak microwave power was not reached during the pulse on-time nor was the microwave power completely turned off during the pulse off-time.

In the nanosecond range, with a pulse duration and repetition time of 54 and 100 nanoseconds respectively, the deposited film was not continuous. An SEM micrograph of the discrete crystallites, with poorly defined faceting, is shown in Figure 2a. With the pulse duration and repetition time increased to 5 and 10 microseconds respectively, the deposited film exhibited mostly (111) faceting as can be seen in Figure 2b. Facets, primarily the (111), were reasonably

formed and typically submicrometer in size. However, some of the (100) facets were found to be 2.5 micrometers in length. The average deposition rate was 0.4 micrometers per hour. In the millisecond pulsed-plasma range, with a 5.6 millisecond pulse duration and a 10 millisecond repetition time, the film exhibited well defined (111) and (100) facets. An SEM micrograph is shown in Figure 2c. The largest (100) facet faces measured 5 micrometers in length. The average deposition rate was 0.8 micrometers per hour. For comparison purposes a film was deposited using a continuous plasma. The SEM micrograph of this film is shown in Figure 2d. As can be seen very well defined (100) and (111) facets are present. The largest (100) facets faces measured 12 micrometers in length. The average deposition rate was 1.5 micrometers per hour.

If we assume that diamond seeding reduces or eliminates the incubation period the average growth rate may be determined from the thickness of the film and the time of deposition. In Table 1, the thickness and growth rate of the deposited films is shown as a function of the pulse period. For the method chosen to calculate the growth rate, i.e., based on film thickness, no growth rate could be assigned to the non-continuous film grown with a plasma generated with nanosecond pulsed microwaves. As can be seen, the thickness of the deposited films by the pulsed-plasma technique increased with the pulse period and reached a maximum with CW plasmas.

Table 1. Thickness and growth rates of pulsed and CW plasma deposited films.

MICROWAVE POWER	film thickness (μm)	film growth rate (μm/hr)
nssec PULSED	NON-CONTINUOUS	—
μsec PULSED	2.5	0.4
msec PULSED	6.0	0.8
CW	10.2	1.5

A Rigaku Rotaflex RU 200B X-ray diffractometer was used to determine the structure and nature of the deposits. X-ray diffraction patterns of the continuous deposited films obtained with plasmas formed with microsecond and millisecond pulsed and CW microwaves are shown in Figure 3. Stick figures of the standard powder pattern of natural cubic diamond are also shown. These define the location and relative intensity of the most prominent cubic diamond crystallographic planes, i.e., (111), (220), (311), (400), and (331) within the diffraction angle of 2 theta that lie between 0 and 140 degrees. The sharp peaks not located at the stick figures are that of the crystalline (100) oriented silicon substrate. Of particular interest is the deviation between the standard powder pattern stick figures relative intensity ratios and that of the intensity ratios of the deposited diamond films. These differences indicated that the deposited

diamond film crystal orientation is non-random and exhibits a preferred texture.

The Raman spectra of continuous films deposited with plasmas formed with microsecond and millisecond pulsed, and CW microwaves were generated by Instruments SA on their Raman Microprobe S3000 spectrophotometer and are shown in Figure 4. Excitation was provided with the 514.5 nm line of an argon ion laser. The film grown with the microsecond pulsed plasma exhibits a very broad non-diamond peak about 1600 cm<sup>-1</sup> above a luminescent background. The nsec pulse film shows a broad diamond peak about 1332.4 cm<sup>-1</sup> and a broad non-diamond peak about 1600 cm<sup>-1</sup>. By comparison, the Raman spectrum of the baseline CW plasma film exhibited a sharp diamond peak with a FWHM of 5.5 at 1333.5 cm<sup>-1</sup> with no other carbon peaks or fluorescent background present. Sharma et al. [7] found that differences in diamond Raman peak location could be attributed to strain in the diamond.

The pulsed plasma average power levels were nearly equal to those used in the baseline CW plasma, however, the use of pulsed plasma with long pulse off-times can result in reduced heating of the substrate. Although this study did not specifically address the optimization of temperature, to determine if a temperature effect did exist with pulsed-plasma depositions, the substrates were heated to 800°C before the plasma was ignited. A less than ten percent improvement in film thickness for the microsecond pulsed-plasma case indicated some substrate cooling had occurred. In this case the deposition temperature could have been optimized for maximum growth, but it was not the primary cause for the lower growth rate.

#### IV. DISCUSSION

Our present understanding of the chemical vapor deposition of metastable phases, such as diamond, is that large deviations from thermodynamic equilibrium exist within the growth environment, and that the metastable phase is kinetically favored has been discussed [8]. The general chemistry of microwave plasma enhanced chemical vapor deposition of diamond with H<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub> as reacting gases is that H, CH<sub>3</sub>, C<sub>2</sub>H, and OH, have been found to be the primary species generated by the plasma. At low CH<sub>4</sub>, C<sub>2</sub>H, and O<sub>2</sub> concentrations the major existing gas species of include H, CH<sub>3</sub>, C<sub>2</sub>H, H<sub>2</sub>O, and CO [9]. In low pressure diamond growth, the methyl radical and acetylene have been identified as the major carbonic growth species. Using isotopic labeling experiments, Chu et al. [10] found that the methyl radical is the primary growth species. Accordingly, in the discussion only methyl radicals are considered, however similar arguments might be made for acetylene radicals. Martin and Hill [11], have reported that methyl radicals and atomic hydrogen have lifetimes in microseconds and seconds respectively. As previously indicated, the gas flows were maintained at constant flow rates during the deposition, and the microwaves were pulsed with approximately 50 percent duty cycles. Based on this understanding and upon the results of this experiment it is proposed that the extent of dissociation of the reactant gases determined the amount and nature of the deposit.

Diamond deposition with plasmas formed with nanosecond pulsed microwaves had the poorest quality. As previously indicated the forward power rise times were on the same order as the pulse duration. During this period, the microwave power did not reach its maximum value limiting the dissociation of

the incoming reactant gases. Scarbrook et al. [5] reported that the dissociation of molecular nitrogen into atomic nitrogen did not reach its maximum concentration until 150 microseconds into the pulse, and indicated that reactant dissociation time, within a plasma, may be dependent on its bond strength. Accordingly, the time it takes to dissociate molecular hydrogen into atomic hydrogen and reach its maximum concentration at the given microwave power, may be on the order of 75 microseconds. For nanosecond pulse periods a low concentration of active species may not provide any significant diamond growth.

In the microsecond pulsed case, the increase of pulse duration to microseconds far exceeded the 40 nanosecond rise time of the microwave system. As a result, sufficient time was available for the microwave forward power to reach its maximum value during the pulse on-time. This allowed for an increase in reactant dissociation greater than could be achieved in the nanosecond case. For the 5 microsecond pulse, the reactant gases could still not reach their maximum concentration if dissociation times are in tens of microseconds. Further, the microsecond pulse off-times are sufficiently long to allow the short lived methyl radicals, formed from the dissociation of methane, to recombine with atomic hydrogen. Methyl radicals must now be generated by hydrogen abstraction of methane with atomic hydrogen. This consumption reduces the number of atomic hydrogen formed [12]. However, the net increase of active species results in an improvement over the nanosecond case.

In the millisecond case, rise time and dissociation time are small compared to the pulse on-time, and the reactants reach their maximum concentration for the given peak power. This maximum concentration of atomic hydrogen coupled with the concomitant increase of atomic hydrogen generated methyl radicals results in an increased growth rate for the film. In the millisecond case, because the generation rate of atomic hydrogen is significantly larger for millisecond than for either nano- or microsecond pulse periods, the amount of atomic hydrogen remaining after recombination is still higher than the other previous pulsed cases. However, the degree of atomic hydrogen supersaturation is dramatically impacted by its recombination during the pulse off-time. As a result, the quality of the film, as represented by the ratio of sp<sub>3</sub> to sp<sub>2</sub> carbon bonds, only moderately improves.

Baseline films obtained with CW formed plasmas had growth rates and film quality that exceeded any obtained from pulsed-plasmas. The extent of dissociation of the reacting gases was dependent upon the microwave forward power and the resultant plasma density, the time of dissociation, and the recombination rates.

The plasma density is a function of the microwave forward power. Although the average power was approximately the same for both the CW and pulsed cases their peak power was not. Pulsed plasmas were operated at near 50 percent duty cycles and their peak power at 2.5 kW was double of that of the CW case. Due to the rise time, only the microsecond and millisecond pulses reached peak power during the pulse period. As a result the plasma density for pulsed cases would be higher than CW cases. However, the plasma density would not have doubled, since the plasma density increases more slowly than the applied forward microwave power.

The time for dissociation impacted the nanosecond and microsecond

pulsed cases, but was not a factor for either the millisecond pulsed or CW cases. Methyl radical recombination was a factor only for microsecond and millisecond pulsed cases. Atomic hydrogen recombination becomes significant only in the millisecond case. In this case, with the increased pulse off-time proportionately more atomic hydrogen recombines, and more significantly atomic hydrogen is not being generated. From the data reported by Martin and Hill [11], it is estimated that for the 5 millisecond off-time there is an 80 percent recombination of atomic hydrogen into molecular hydrogen. For the experimental conditions used, CW plasmas produced a higher rate of reactant gas dissociation than any of the pulsed cases. As a result the growth rate and quality of CW films were higher than pulsed plasma films.

As seen in Figure 2, the crystal facets increase in size and appearance as the pulse on-time increases. Crystal faceting can also be considered a measure of film quality. Harker and DeNatale [13], noted that an increase in the oxygen content of the reacting gases resulted in improvements in reactive etching rates, which increased the diamond crystallite size. The possibility of depositing diamond layers with pulse on-times and non-diamond carbon during pulse off-times was considered. However, with subsecond pulse cycles and deposition rates at less than an angstrom per second, atomic layering could not be possible. As a result, it was concluded that diamond and non-diamond carbon are deposited simultaneously.

Because of the fixed composition of the incoming reactant gases, improvements in growth rates could in part be attributed to an increase in the oxygen dissociation of the carbon precursor methane. However, due to the short lifetime of methyl radicals, the mechanism of hydrogen abstraction is needed to generate these radicals. Although oxygen has been shown to improve both the deposition rate as well as the quality of the film, it requires the presence of atomic hydrogen. Of the roles ascribed to oxygen by Spear and Frenklach [14], only that of promoting the gas phase production of hydrogen would apply to improving the growth rate of diamond films. It was first reported by Spitsyn et al. [15] that atomic hydrogen directly contributes to both the quality as well as the growth rate by stabilizing the diamond surface, preferentially etching sp and sp<sup>2</sup> bonded carbon from the growing surface, and activating the growth surface by hydrogen abstraction. The improvement in diamond film growth for increasing pulse periods which reached a maximum for CW grown films, would support the idea that these improvements were attributed primarily to increases of atomic hydrogen. For a given ratio of hydrogen and methane, once the supersaturated level of hydrogen is reached, diamond is deposited. Once diamond growth is achieved, increasing the atomic hydrogen by only a small factor will significantly improve the growth rate and quality. This is in qualitative agreement, for the low pressure regime portion of the theory proposed by Vandenbulcke et al. [16], which concerns the effects of atomic hydrogen supersaturation on the growth of diamond.

experimental conditions used, the diamond films' growth rates and quality improved with increasing pulse duration, and reached a maximum with CW generated films. This was attributed primarily to an increasing degree of supersaturation of atomic hydrogen at the growth surface with increasing pulse duration.

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#### REFERENCES

1. S. Matsumoto, J. of Mat. Science Letters, **4**, 600 (1985).
2. K. Kitahama, K. Hirata, H. Nakamatsu, S. Kawai, T. Imai, N. Fujimori, Y. Yoshino, and A. Doi, Appl. Phys. Lett., **49**, 643 (1986).
3. K. Suzuki, A. Sawabe, H. Yasuda, and T. Inuzuka, ibid., **50** (12), 728 (1987).
4. M. Kano, Y. Sato, S. Matsumoto, N. Setaka, J. Crystal Growth, **62**, 642 (1983).
5. G. Scarbrook, I. P. Llewellyn, S. M. Ojha, and R. A. Heinecke, the Proc. of EVAC-88, Vacuum, **8** (8/9), 627 (1988).
6. M. Akluft and D. Brock, Pro. 1st Internat. Sympos. on Diamond and Diamond-Like Films, Electrochim. Soc., **89** (12), 114 (1989).
7. S. K. Sharma, H. K. Mao, P. M. Bell, and J. Z. Xu, J. Raman Spectra Res., **5**, 2405 (1990).
8. R. C. DeVries, Ann. Rev. Mater. Sci., **17**, 161 (1987).
9. T. Kawato and K. Kondo, Japan. J. Appl. Phys., **26** (9), 1429 (1987).
10. C. J. Chu, M. P. D'Evelyn, R. H. Haug, and J. L. Margrave, J. Mater. Res., **16**, 350 (1985).
11. L. R. Martin and M. W. Hill, Pro. 1st Internat. Sympos. on Diamond and Diamond-Like Films, Electrochim. Soc., **89** (12), 568 (1989).
12. J. E. Butler and F. G. Celli, ibid., **89** (12), 317 (1989).
13. A. B. Harker and J. F. DeNatale, J. Mater. Res., **5**, 818 (1990).
14. K. E. Spear and M. Frenklach, Pro. 1st Internat. Sympos. on Diamond and Diamond-Like Films, Electrochim. Soc., **89** (12), 122 (1989).
15. B. V. Spitsyn, L. L. Bouillov, and B. V. Deryagin, J. Cryst. Growth, **53**, 219 (1981).
16. L. Vandenbulcke, P. Bou, and G. Moreau, Pro. 1st Internat. Sympos. on Diamond and Diamond-Like Films, Electrochim. Soc., **89** (12), 594 (1989).

#### V. SUMMARY AND CONCLUSIONS

Diamond films were grown in plasmas formed with microwaves that were modulated with a pulse generator. Films obtained with the use of cycle times in nanosecond, microsecond, and millisecond ranges with 50 percent pulse on-times were compared to baseline films which were obtained with a CW plasma. For the

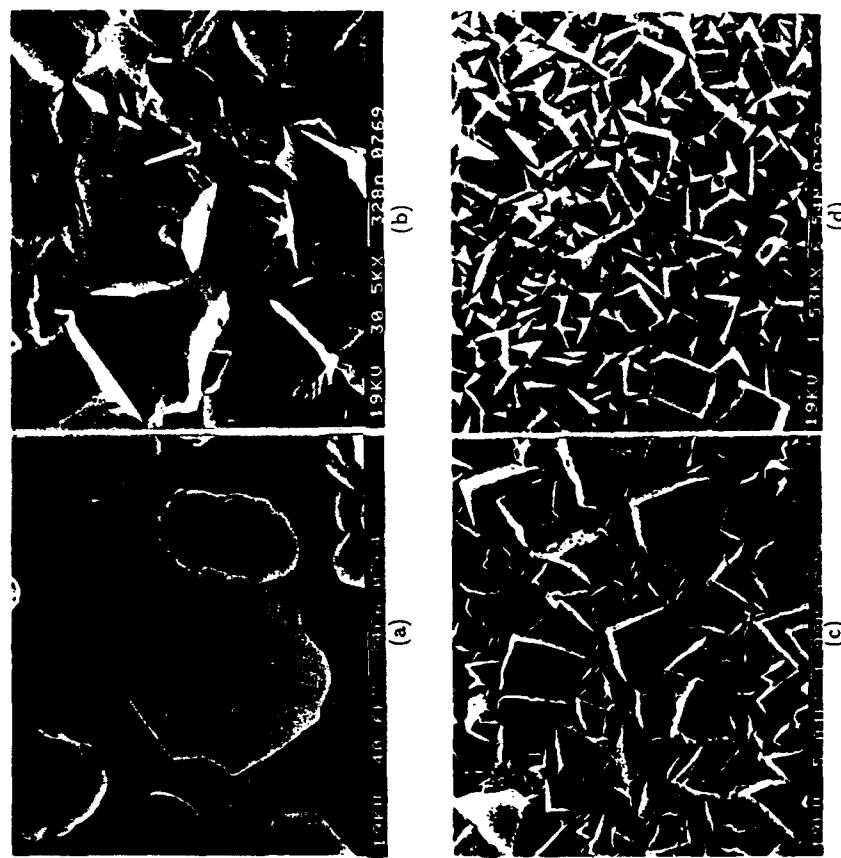


Figure 2. SEM microphotographs of deposited diamond films. (a) nanosecond pulsed-plasma; (b) millisecond-pulsed plasma; (c) CW plasma baseline.

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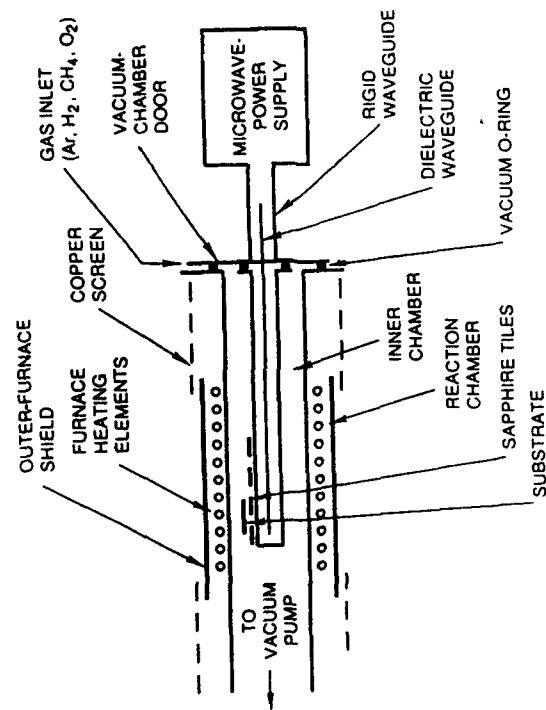


Figure 1. Schematic drawing of the pulse/CW plasma deposition system.

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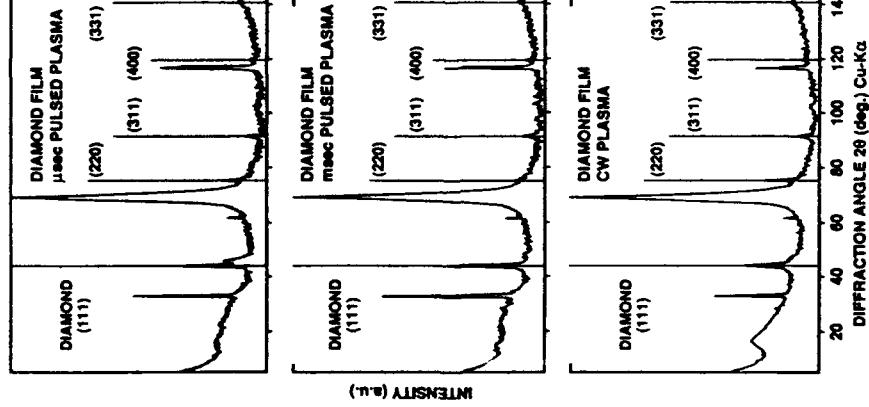


Figure 3. XRD pattern of microsecond and millisecond pulsed, and CW plasma deposited diamond film.

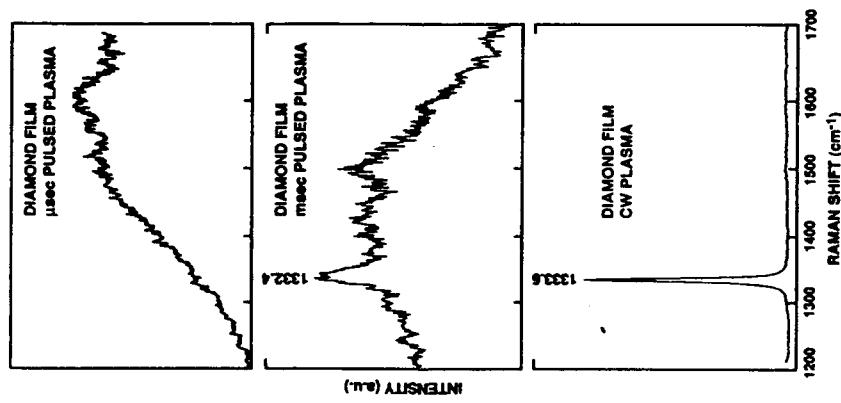


Figure 4. Micro-Raman spectra of microsecond and millisecond pulsed, and CW plasma deposited diamond film.

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Publications

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